

COATINGS. ENAMELS

UDC 539.216.2:666.113.81'28(047)

STRUCTURE OF THIN FILMS OF BINARY AND MULTI-COMPONENT LEAD SILICATE GLASSES ON METALS

O. M. Kanunnikova,¹ F. Z. Gil'mutdinov,¹ S. F. Lomaeva,¹ and O. Yu. Goncharov¹Translated from *Steklo i Keramika*, No. 3, pp. 28–32, March, 2003.

The topography and composition of surface layers in thin films of lead silicate glasses obtained by thermodiffusion homogenization on metal substrates is investigated. The composition of the film – substrate transitional layer is analyzed.

Lead silicate glasses of various compositions are used to produce microchannel plates. It is known that industrially melted glass has a complex heterogeneous structure. In melting glass of the $\text{PbO} \cdot \text{SiO}_2$ composition close to lead metasilicate, infrared spectroscopy can identify metasilicate, orthosilicate, and other small areas in massive glass, whose concentration depends not only on the melting procedure but on the batch prehistory as well [1]. In various thermal-treatment procedures some areas may grow to microliquescent inclusions, which significantly modify the emission properties of the surface. Apparently the reason for this is the substantial viscosity of the melts, as a consequence of which absolute mixing does not occur in melting and initial conglomerates can exist sufficiently long. These films are more homogeneous in their composition. One of the methods for producing thin melts is thermal diffusion synthesis from respective element layers alternately deposited on a substrate until reaching a required total thickness and simultaneous or subsequent thermal homogenization.

The present study investigated thin films of lead silicate glasses obtained by thermodiffusion homogenization. The ratios of oxides deposited on a metal substrate correlated with glass compositions (here and elsewhere molar content, unless otherwise specified) of grades MKO-20 ($40.0\text{PbO} + 60.0\text{SiO}_2$) and 6Ba4 ($64.0\text{SiO}_2 + 16.8\text{PbO} + 4.3\text{BaO} + 11.0\text{Na}_2\text{O} + 3.2\text{Al}_2\text{O}_3$). Materials selected for substrates were copper, aluminum, aluminum bronze, and ferrochromium steel. Residual pressure in the spraying chamber was 10^{-5} Pa. Partial layers of alternately deposited oxides have

an effective thickness of about 0.2 single layer. The homogenization temperature was 773 K [2].

X-ray electron studies were carried out on an ES-2401 spectrometer. Spectra were excited by MgK_α radiation and processed using the method in [3]. Mass-spectrometric analysis was carried out on an MS-7201 spectrometer. The surface topography was investigated on an R-47 atomic force microscope in a semicontact regime in air using a needle produced by the NT MDT Company.

The composition and chemical state of film components determine their emission capacity, i.e., the secondary electron emission coefficient. The mechanism of secondary electron emission is studied in [4, 5]. The authors developed a theory of a plasmon mechanism of secondary emission of electrons by dielectrics, in which the main role is attributed to the process of generation and disintegration of plasmons arising as a consequence of inelastic interaction of primary electrons with the electron structure of solids. The probability of plasmon excitation depends on the concentration of valence electrons and the minimum energy required for excitation of valence electrons. The latter is approximately equal to the forbidden-band width. The coefficient of secondary electron emission can be found from the following formulas:

$$\sigma(x) = \sigma(0) \frac{hw(x) \ln [\ln E_p / (hw(x))]}{hw(0) \ln [E_p / (hw(0))]};$$

$$hw^2(x) = hw^2(0) \frac{N(x)[\rho(x)/\mu(x)]}{N(0)[\rho(0)/\mu(0)]},$$

where $\sigma(x)$ is the coefficient of secondary electron emission of glass with a PbO content equal to x ; $\sigma(0)$ is the coefficient

¹ Udmurtian State University, Izhevsk, Russia; Physicotechnical Institute of the Ural Branch of the Russian Academy of Sciences, Ekaterinburg, Russia.

of secondary electron emission of vitreous SiO_2 , $\sigma(0) = 3.6$; $hw(0) = 22.5$ [5]; E_p is the energy of primary electrons, at which a maximum $\sigma(x)$ is registered; $\rho(0)$ and $\rho(x)$ are the densities of quartz (2.22 g/cm^3) and glass; $\mu(0)$ and $\mu(x)$ are the molar masses of quartz and glass.

The electron contributions of various atoms to the glass structure are calculated from the formula

$$N(x) = N(\text{Si}) + N(\text{O}_{\text{Si-O-Si}}) + \\ N(\text{O}_{\text{Pb-O-Pb}}) + N(\text{O}_{\text{Pb mod}}) + N(\text{Pb}),$$

where $N(\text{Si}) = 4(1-x)$ is the silicon in silicon-oxygen chains; $N(\text{O}_{\text{Si-O-Si}}) = 4\alpha(2-x)$ is the bridge oxygen in the Si-O-Si bond; $N(\text{O}_{\text{Pb-O-Pb}}) = 4\gamma(2-x)$ is the bridge oxygen in the Pb-O-Pb bond; $N(\text{O}_{\text{Pb mod}}) = 4\beta(2-x)$ is the oxygen in bonds with the modifying lead ion; $N(\text{Pb}) = 4\tau x$ is the lead in a covalent bond with oxygen; x is the content of lead oxide; α , β , γ , and τ are shares of atoms in a respective chemical state in the total number of atoms of the given type (based on results of decomposition of x-ray electron spectra).

Using these formulas, Shakhmin [5] determined the coefficients of secondary electron emission for lead silicate glasses. A good qualitative correlation was obtained between experimental and estimated variation regularities of the secondary electron emission coefficient on varying the lead oxide content in glasses (Table 1). This corroborates the validity of the theory proposed in [4, 5] and the possibility of predicting values of the secondary electron emission coefficient in glasses depending on the glass composition and structure.

However, there are quantitative differences that grow from 10% for low-lead glasses to 25% for high-lead glasses. The reason for this consists of the choice of nuclei for decomposition of the O 1s and Pb 4f spectra. It was a priori assumed in [5] that oxygen atoms in vitreous quartz and lead atoms in glass with a 30% content of PbO exist in a unique chemical state; hence the O 1s spectrum of vitreous quartz and Pb 4f spectrum of glass $30\text{PbO} + 70\text{SiO}_2$ were selected as nuclei for decomposition. It is impossible to accept this assumption, as it is known that oxygen atoms in all modifications of quartz can exist in two positions that are at different distances from the bridge or end silicon atoms [6]. The existence of an inverse proportionality between the bond energy (O 1s) and the distance between the oxygen atom and the element bonded to it [7] implies that the O 1s spectrum consists of two components, whose ratio of internal intensities is approximately equal to the ratio of the quantities of the bridge and end oxygen atoms.

There is no reason to assume either that lead atoms in glass with 30% lead oxide exist in a unique chemical state. To select a nucleus for decomposition of the Pb 4f line, we decomposed the spectrum of crystalline lead orthosilicate with a known structure, in which there are two types of lead atoms with different types of interaction with silicon and oxygen [8]. In decomposing the Pb 4f spectrum we isolated two

TABLE 1

Molar content of PbO, %	Secondary emission coefficient of glass			Relative content of modifying lead, %	
	data in [5]	estimated data [5]	our data	data in [5]	our data
30.0	2.77	3.04	2.77	100.0	80.0
40.0	2.67	3.04	2.65	95.0	75.0
50.0	2.64	2.99	2.63	86.7	48.0
55.0	2.57	2.98	2.59	88.3	35.0
66.7	2.30	2.92	2.31	65.8	10.0

components and hereafter in decomposing glass and film spectra we used a nucleus whose width is approximately equal to the width of these two components. Table 1 lists the results of estimation of secondary electron emission coefficients for binary lead silicate glasses implemented by decomposition of Pb 4f and O 1s spectra. According to the data in [5], the relative content of modifying lead is substantially overestimated, i.e., the coefficient τ in the calculation formula for N_x is overestimated, which is the main reason for the elevated values of σ_{est} . The values of secondary electron emission coefficients calculated by us agree well with experimental data. This suggests that estimated coefficients of secondary electron emission of films will also be close to experimentally measured values.

Films MKO-20. It was earlier shown for massive glasses that thermally stimulated processes in binary lead-silicate glasses are oriented to the minimums on the liquidus curve in the phase diagram of $\text{SiO}_2 - \text{PbO}$ [9]. The composition of MKO-20 glass correlates with the minimum on the specified curve; therefore, diffusion processes in heating in this system are insignificant (Table 2). The low content of PbO in film is related to the high pressure of the vapor of this oxide [10]: the greater part of it evaporates in heating. The chemical state of residual lead in MKO-20 films is similar to that in massive glasses: modifying lead and glass-forming lead are observed, although the quantity of glass-forming lead in films is lower than in mass samples (fractures) and decreases even more with a decreasing thickness of glass. The relative quantity of bridge oxygen is high, which suggests the vitreous state of the deposited film.

Films 6Ba4. Thermally stimulated processes in glass of complex composition can be predicted based on analysis of phase diagrams $\text{SiO}_2 - \text{Al}_2\text{O}_3$, $\text{SiO}_2 - \text{Na}_2\text{O}$, $\text{SiO}_2 - \text{BaO}$, and $\text{SiO}_2 - \text{PbO}$. Heating a massive sample enriches its surface with lead and aluminum and depletes it of barium and sodium.

Compositions of films 6Ba4 are given in Table 3. The content of aluminum is elevated, the degree of concentration growing as the film thickness decreases. This is due to diffusion of not only deposited aluminum oxide, but also of metallic aluminum from the substrate toward the surface. The surface layers of film are depleted of barium and sodium. Lead oxide depletion is due to its evaporation in thermal homogenization.

TABLE 2

Film thickness, Å	Substrate	Silicon		Lead		Secondary emission coefficient	Composition of surface layer, molar content, %
		bond type	relative content, %	chemical state	relative content, %		
3000	Steel	Si – O – Si	63.8	Modifier	73.7	3.57	6PbO + 94SiO ₂
		Si – O – Pb	28.4	Glass former	20.6		
		SiO ₂	7.9	Metal	4.7		
1000	The same	Si – O – Si	50.3	Modifier	79.9	3.47	8PbO + 92SiO ₂
		Si – O – Pb	29.4	Glass former	11.3		
		SiO ₂	20.3	Metal	8.9		
500	"	Si – O – Si	43.3	Modifier	75.6	3.07	20PbO + 80SiO ₂
		Si – O – Pb	34.6	Glass former	19.0		2.5Fe* (Fe ₂ O ₃ , FeO, Fe)
		Si – O – Fe	17.1	Metal	5.4		
		SiO ₂	5.0				
200	"	Si – O – Si	52.2	Modifier	88.2	2.60	29PbO + 71SiO ₂
		Si – O – Pb	37.2	Glass former	7.0		9.6Fe* (Fe ₂ O ₃ , FeO, Fe)
		Si – O – Fe	4.8	Metal	4.8		
		SiO ₂	5.4				
200	Copper	Si – O – Si	63.0	Modifier	63.3	–	26PbO + 74SiO ₂
		Si – O – Pb	27.0	Glass former	28.2		14Cu*
		Si – O – Cu	10.0	Metal	8.5		
500	Bronze	Si – O – Si	66.4	Modifier	70.7	3.06	30PbO + 70SiO ₂
		Si – O – Pb	23.8	Glass former	18.3		8Cu*
		Si – O – Cu	7.8	Metal	10.0		
		SiO ₂	2.0				

* Atomic content.

The surface topography of films 6Ba4 of thickness 500 and 1000 Å on bronze and steel is shown in Fig. 1. The film thickness has virtually no effect on the surface topography. Surface roughness of the metal substrate facilitates the formation of conical heterogeneities on the film surface up to 100 nm high and 400 – 500 nm in the diameter of the base (Fig. 2). These heterogeneities do not have a fine structure and their height and shape do not depend on the substrate material. They presumably originate in heat treatment as a consequence of a reaction between the oxides deposited.

The surface of films deposited on smoother substrate areas is made up of spherical structures sized 20 – 80 nm protruding above the surface to a height of 1.5 – 3.0 nm and cells of the same size. Analysis of the surface under a two-pass phase-contrast regime (Fig. 3) demonstrated that the surface layer of 6Ba4 films is not homogenous in its phase composition, i.e., the spherical structures correlate with different phases. Phases of different composition and cells are uniformly distributed over the surface. It is clear that in this case the initial components have not fully reacted. The cells

TABLE 3

Film thickness, Å	Substrate	Silicon		Lead		Composition of surface layer, molar content, %
		bond type	relative content, %	chemical state	relative content, %	
1500	Steel	Si – O – Si	66.1	Modifier	25.6	83.6SiO ₂ + 1.8PbO + 1.0BaO + 6.2Na ₂ O + 7.3Al ₂ O ₃
		Si – O – Al, Pb	23.1	Glass former	74.4	
		Si – O – Ba, Na	10.7			
500	The same	Si – O – Si	60.0	Modifier	28.0	83.3SiO ₂ + 2.6PbO + 2.3BaO + 5.5Na ₂ O + 11.5Al ₂ O ₃ , Fe traces
		Si – O – Al, Pb	25.0	Glass former	72.0	
		Si – O – Ba, Na	15.0			
200	"	Si – O – Si	53.0	Modifier	58.0	78.5SiO ₂ + 1.9PbO + 2.1BaO + 3.4Na ₂ O + 15.0Al ₂ O ₃ , 6Fe*
		Si – O – Al, Pb	29.1	Glass former	42.0	
		Si – O – Ba, Na	15.9			
1000	Bronze	Si – O – Si	70.0	Modifier	31.6	84.3SiO ₂ + 2.5PbO + 1.8BaO + 6.7Na ₂ O + 4.7Al ₂ O ₃
		Si – O – Al, Pb	22.5	Glass former	68.4	
		Si – O – Ba, Na	7.5			

* Atomic content.

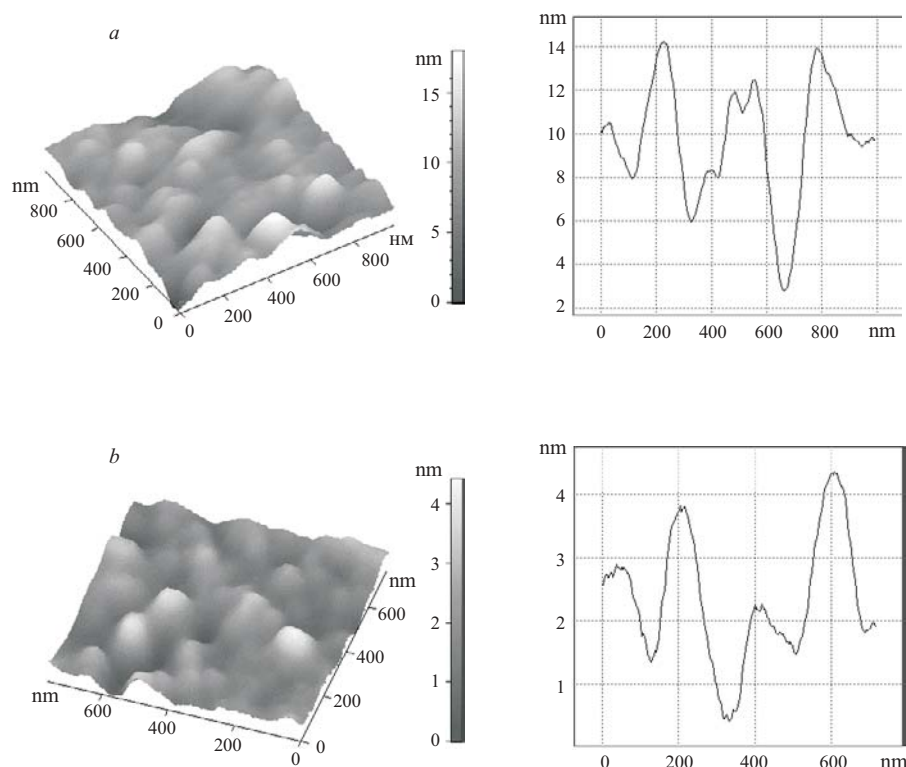


Fig. 1. ASM image of 6Ba4 films 500 Å thick on bronze (a) and 1000 Å thick on steel (b).

have originated as a result of evaporation of spray-deposited lead oxide under heat treatment.

Interface boundaries. The composition of the layer on the film – substrate interface depends on the reaction of spray-deposited oxides with the substrate material. A thermodynamic analysis was performed according to a method based on finding the extremum of the system entropy while satisfying a number of boundary conditions, implemented as an ASTRA program. The following conditions were selected: temperature 773 K; residual air pressure 10^{-5} Pa. Due to the absence of thermodynamic data, the possibility of copper silicate formation was disregarded.

Table 4 shows compositions of intermediate layers obtained on the basis of x-ray electron and thermodynamic analysis. Apart from compounds formed as solid phases, the composition of the gaseous phase was identified. The gaseous phase is mainly formed from metallic lead and lead oxide (in the form of monomers PbO and dimers Pb_2O_2), whose quantity depends on the temperature of the substrate, the pressure, and the composition of the residual atmosphere in the spraying chamber. The ratio of lead to lead oxide is approximately 1 : 100. The results of x-ray electron analysis agree with the thermodynamic calculation.

According to the data of mass-spectrometry analysis, the transitional-layer thickness is 100 – 120 Å. The thickness of the layer subjected to x-ray electron spectroscopy is greater than that of massive samples. This one of the reasons for the difference between estimated and experimentally determined

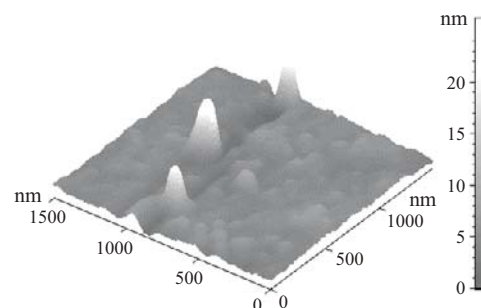


Fig. 2. Conical heterogeneities on the surface of film 6Ba4 of thickness 1000 Å.

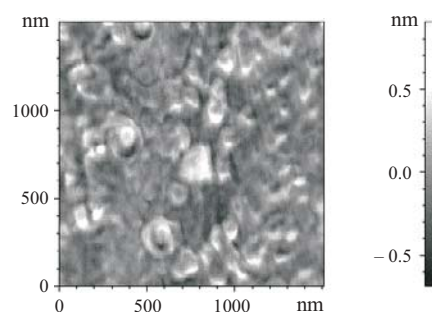


Fig. 3. Image of the surface of 6Ba4 film 1000 Å thick in the phase-contrast regime.

samples. Another reason is that the process kinetics is not taken into account in thermodynamic calculations.

TABLE 4

Composition of substrate, atomic content, %	Composition of deposited layer, molar content, %	Composition of intermediate layer	
		thermodynamic analysis, molar content, %	x-ray electron analysis, atomic content, %
Cu	40PbO + 60SiO ₂	90.1CuO, 6.3SiO ₂ , 3.6PbO	1.8Pb, 23.9Si, 34.6O, 39.7Cu
Cu + 2.0Al	40PbO + 60SiO ₂	89.2CuO, 6.3SiO ₂ , 3.6PbO, 0.9Al ₂ O ₃	1.3Pb, 16.2Si, 2.9O, 75.0Cu, 5.4Al
73.8Fe + 11.4Ni + 8.0Cr + 0.3Ti + 6.4Al	40PbO + 60SiO ₂	2.6 Al ₂ O ₃ , 52.6SiO ₂ , 0.2PbO, 6.6NiO, 18.4Fe ₂ O ₃ , 3.3Cr ₂ O ₃	0.7Pb, 11.5Si, 7.8O, 41.2Fe, 8.0Al, 8.2Ni, 2.0Cr
Cu + 2.0Al	64.0SiO ₂ + 16.8PbO + 4.3BaO + 11.0Na ₂ O + 3.2Al ₂ O ₃	29.7SiO ₂ , 1.1Si ₃ N ₄ , 0.8Al ₂ O ₃ , 27.0Cu, 27.0CuO, 13.5Pb, 0.8PbO	9.8Si, 0.4Pb, 0.4Ba, 0.7Na, 21.1O, 60.0Cu, 7.0Al
73.8Fe + 11.4Ni + 8.0Cr + 0.3Ti + 6.4Al	The same	63.8SiO ₂ , 3.2Si ₃ N ₄ , 2.3Fe ₂ O ₃ , 2.6Fe, 1.3NiO, 2.8Al ₂ O ₃ , 0.5Cr ₂ O ₃ , 5.1Na ₂ Si ₂ O ₅ , 1.5BaSiO ₃ , 12.8Pb, 3.8PbO	0.8Si, 0.2Pb, 0.3Ba, 0.5Na, 7.8O, 56.2Fe, 12.7Al, 1.1Cr

Thus, the composition of the surface layers of silicate glass films produced by thermodiffusion homogenization depends on the pressure ratio of the vapor of spray-deposited oxides at the homogenization temperatures and the direction of thermodiffusion processes: the composition of lead-silicate glass films in general is significantly depleted of lead oxide due to its evaporation, and depletion of the surface layers in barium and sodium oxides is due to the diffusion processes. With a film thickness of 500 Å or more the composition of the surface layer virtually does not depend on the substrate material.

The chemical states of the surface-layer components in binary lead-silicate film over 500 Å thick are similar to the states of glasses of the same composition.

An intermediate layer is formed at the film – metal substrate interface, its composition depending on the chemical reaction between spray-deposited oxide and the substrate material. The thickness of this layer is 100 – 150 Å.

The film topography depends on the macroheterogeneities of the metal substrate.

The secondary electron emission coefficients of binary lead silicate glass films obtained by thermodiffusion homogenization are close to analogous coefficients of massive glasses of the same composition.

REFERENCES

1. *IR Spectra of Inorganic Glasses* [in Russian], Khimiya, Moscow (1972).
2. O. M. Sorokin, L. V. Bulycheva, and I. I. Morkovina, "Studies of thermally homogenized layers of PbO and SiO₂ oxide mixtures using the UV photoelectron spectroscopy method," *Fiz. Khim. Stekla*, **12**(1), 62 – 68 (1986).
3. V. I. Povstugar, A. A. Shakov, S. S. Mikhailova, et al., "Decomposition of complex x-ray electron spectra using the fast discrete Fourier transform and an improved convergence procedure," *Zh. Anal. Khim.*, **53**(8), 795 – 799 (1998).
4. A. I. Gusarov, V. L. Mashkov, and A. M. Tyutikov, "On additivity of secondary electron emission in lead silicate glasses," *Fiz. Khim. Stekla*, **13**(1), 34 – 43 (1987).
5. A. L. Shakhmin, *Electron Structure of Lead Silicate Glasses and Its Correlation with the Coefficient of Secondary Electron Emission, Author's Abstract of Candidate's Thesis* [in Russian], St. Petersburg (2000).
6. F. Libau, *Structural Chemistry of Silicates* [Russian translation], Mir, Moscow (1988).
7. V. I. Nefedov, D. Gati, B. F. Dzhurinskii, et al., "X-ray electron studies of oxides of some elements," *Zh. Neorg. Khim.*, **XX**(9), 2307 – 2314 (1975).
8. K. Kato, "Die OD-structur von bleisilicat Pb₂SiO₄ und bleisilicat – germanat – mischkristall Pb₂(Si, Ge)O₄," *Acta Cryst.*, **36**, 2539 – 2545 (1980).
9. M. F. Sorokina, O. M. Kanunnikova, F. Z. Gil'mutdinov, and V. I. Kozhevnikov, "X-ray electron study of reduction of lead silicate glasses under heating in hydrogen," *Neorg. Mater.*, **33**(5), 621 – 627 (1997).
10. N. N. Sevryukov, *Metallurgy of Nonferrous Metals* [in Russian], Metallurgiya, Moscow (1969).